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# Oil Recovery from Petroleum Sludge by Solvent Extraction

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**Abstract:** Technical problems associated with sludge deposition in storage units of petroleum industries are enormous. The conventional methods of management are laborious and uneconomical; the hydrocarbon contents are lost to the pits, causing environmental problems. Solvent recovery of the hydrocarbons from accumulated sludge in storage facilities of oil industries in the Niger delta area of Nigeria was carried out. A recovery of about 67.5% hydrocarbon oils was obtained, out of which 86.7% were aromatic. Gas chromatographic analysis of the extracted oil showed it contained the hydrocarbons in the range of $C_9$–$C_{25}$, which is good petrochemical industry feedstock. Hexane and xylene showed high potentials for hydrocarbon oil extraction from the sludge, reducing the quantity of solid waste to the barest minimum.

**Keywords:** aromatic sludge, extractable hydrocarbon oil, sludge disposal

## INTRODUCTION

Petroleum industries generate large quantities of sludge (Jean et al., 2001) that accumulate in crude oil tanks, refinery products tanks, desalters, and elsewhere during oil production and processing (Kurakos and Manjooran, 2001). Petroleum sludge is a complex mixture containing different quantities of waste oil, wastewater, sand, and mineral matter. Petroleum industries are burdened with the problem of handling the large quantities of sludge generated, a major source of environmental pollution (Asia et al., 2006). An economical process of managing the sludge requires reliable characteristic data.

Recycling is the most desirable environmental option for handling oily sludge, due to the possibility of recovering valuable oil for reprocessing,

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reformulating, or energy recovery (Elektorowicz and Habibi, 2005). There is a basic need to increase energy efficiency by sustainable growth. Presently, easy and economically efficient technologies for oil sludge treatment to recover valuable fuel oil have not been found. Universally applicable technology for treatment of petroleum sludge should be developed to recover petroleum in a form suitable for direct processing in the refinery to high quality petroleum products.

Due to the changes in the chemical and physical composition of the oil in the sludge associated with refining processes and blending (Schmidt, 1986), information on the compound types and their distribution in oil sludge is necessary for developing the basic compositional data needed for the efficient processing and use of these materials. Thus, meaningful evaluation of the extent of sludge treatment before disposal could be done and can make significant impact on refinery and petrochemical industries.

The thrust of this study is to determine the physical and chemical properties of oil sludge from the Escravos oil field in the Niger Delta of Nigeria, evaluate the performance of petroleum based solvents for extraction of valuable petroleum oil from the sludge sample, and analyze the constituents' hydrocarbons.

## EXPERIMENTAL

The petroleum oil sludge used for this study was obtained from the Escravos oil field in Niger Delta of Nigeria.

Water content: The American Society for Testing and Materials (ASTM) standard method D95 was used for measuring the water content of the oily sludge. The oily sludge was heated with benzene (solvent) which co-distilled with the water in the sample in a fume cupboard. Condensed solvent and water were continuously separated in a trap, and the water settled as the bottom layer. The condensed liquid containing water and hydrocarbon was transferred to a graduated cylinder. A water layer with higher density was at the bottom of the cylinder. The volume of the water was then used in calculating the water content in the sample (using the density of water of 1 g/cm$^3$).

Volatile hydrocarbon content: A known mass of sample was put in an oven (with ventilation) at 105°C for 24 hours. The reduction in mass indicated the moisture and light hydrocarbon content in the sludge. As water content was measured previously, the light hydrocarbon content (in wt.%) was calculated as follows:

$$\text{Light hydrocarbon} = \frac{\text{reduced mass, g}}{\text{mass of tested sample, g}} \times 100\% - \text{water content wt.\%} \quad (1)$$

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Solid content: Dried samples (105°C) were placed in a furnace at 550°C for 30 mins. The residue was weighed. The solids content of the sludge was calculated in weight percent using the equation:

$$\text{Solid content} = \frac{\text{mass of residue remaining after burning, g}}{\text{mass of tested sample, g}} \times 100\% \quad (2)$$

Nonvolatile hydrocarbon content: After measuring the water content, light hydrocarbon content, and solid content, the nonvolatile hydrocarbon content can be calculated in weight percent as follows:

$$\text{NVH} = 100\% - \text{VH} + \text{SC} + \text{WC} \quad (3)$$

where NVH is nonvolatile hydrocarbon (wt%)
VH is volatile hydrocarbon content (wt%)
SC is solid content (wt%)
WC is water content (wt%)

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## Petroleum Sludge Extraction

Total petroleum hydrocarbon (TPH) was extracted from the petroleum sludge using a sequential shaking extraction (Schwab et al., 1999). The petroleum sludge was air-dried and mechanically ground to pass through a 0.25 mm mesh sieve. 5 g of air-dried petroleum sludge was spiked with 500 mL of solvent and agitated on reciprocal shaker for 30 min, and then centrifuged at 2000 rpm for 10 min to settle the petroleum sludge. The supernatant was collected in 60 mL glass jars. This procedure was repeated two more times, and the mass of the final extractant was recorded. The supernatant solution was left for 1 hr to allow for phase separation. The organic phase was collected and stored for further analysis. A 1.5 mL sample was transferred into a 2-mL gas chromatography (GC) vial, spiked with 10 $\mu$L of 1000 mg/L $\alpha$-androstane, capped with a Teflon-lined septa, and stored at 4°C until analysis by GC.

### Gas Chromatographic Analysis

All the extracted samples were analyzed on a Hewlett-Packard 5890A gas chromatograph, equipped with a flame ionization detector (FID) and a HP7673A auto sampler utilizing a DB-TPH column. The DB-TPH column, designed specifically for analysis of TPH, had an inside diameter of 0.32 mm, a length of 30 m, and a 0.25 $\mu$m film thickness. The fuel and carrier gas for the FID was $H_2$. The carrier gas was delivered at 67 $\mu$L $s^{-1}$ and the fuel gas at 670 $\mu$L $s^{-1}$. Nitrogen was used as the make-up gas at a flow rate of 530 $\mu$L $s^{-1}$. Air was supplied as the oxidant at a rate of 7.0 $\mu$L $s^{-1}$. The initial oven temperature was maintained at 40°C for 2 min, and then increased

**Table 1.** Properties of sludge sample

| Properties | Values |
|---|---|
| Specific gravity @ 29°C | 0.885 |
| Specific gravity @ 15.6°C | 0.894 |
| API gravity | 26.768 |
| Viscosity @ 24°C | 289.676 |
| Water content (%) | 18.910 |
| Solid content (%) | 7.85 |
| Volatile hydrocarbon content | 45.84 |
| Non-volatile hydrocarbon content | 27.40 |

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at a rate of 0.2°C $s^{-1}$ until attainment of 320°C. It was then maintained at 320°C for 10 min. Injection port temperature and detector temperature were 250°C and 350°C, respectively. The split less injection volume was 2 $\mu$L. The TPH concentrations were measured using integrated GC areas and then converted to concentrations using external standard calibration curves.

## RESULTS AND DISCUSSION

The properties of the sludge sample are reported in Table 1. The data indicate that the sludge is aromatic, since the value of the API gravity is less than 33 (Bhaskara, 1990). The effectiveness of the separation of the recyclable components using different solvents is reported in Table 2. Hexane shows the highest performance in extracting useful hydrocarbon from the sludge. The optimum sludge/solvent ratio for the hydrocarbon extraction is reported in Figure 1, while various components of extracted hydrocarbon oil are shown in Figures 2 to 4.

**Table 2.** Sludge property variation with extraction solvents

| Properties | Hexane | Xylene | Kerosene | Ethyl acetate |
|---|---|---|---|---|
| *Aqueous liquid, % | 27.08 | 29.03 | 28.55 | 27.87 |
| *Solid content, % | 5.44 | 5.6 | 8.9 | 10.64 |
| *Hydrocarbon oil content, % | 67.48 | 65.38 | 62.55 | 63.94 |
| Chemical | | | | |
| Aliphatic content, % | 13.31 | 44.955 | | |
| Aromatic content, % | 86.69 | 55.05 | | |
| Aromatic-Aliphatic ratio | 6.51 | 1.22 | | |

*Average value

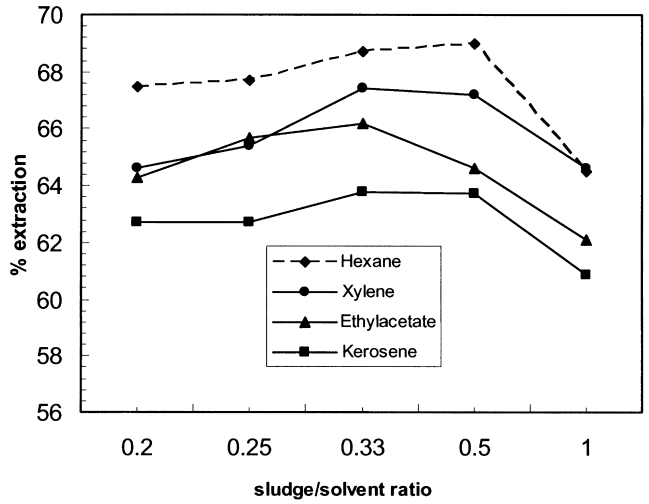


***Figure 1.*** Variation of % extraction of hydrocarbon from sludge with sludge/solvent ratio.

From Table 1, the sludge contained a high amount of light hydrocarbon. The accumulated sludge matrix at the base of the storage tank is prevented from evaporation since it is secluded from contact with moving air by virtue of its location. The extractable hydrocarbon oil comprises about 73.24% of the sludge, containing both volatile and non-volatile hydrocarbons. Preliminary evaluation of the four solvents (hexane, xylene, ethylacetate and kerosene) for extraction of petroleum hydrocarbon from sludge shows hexane as having the highest extraction ability, extracting about 67.48% of the hydrocarbon

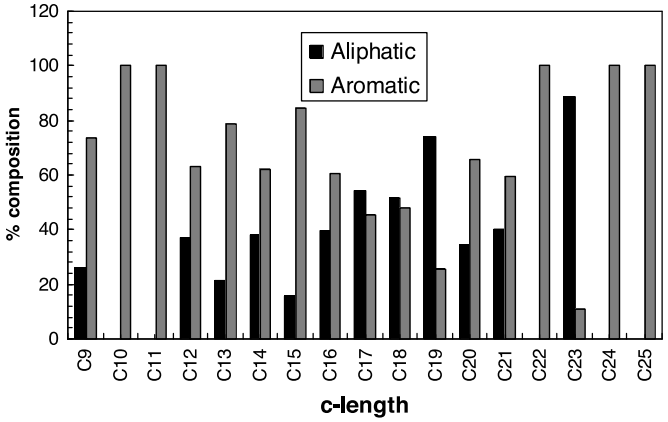


***Figure 2.*** Aromatic-aliphatic distribution in extracted oil from the sludge.

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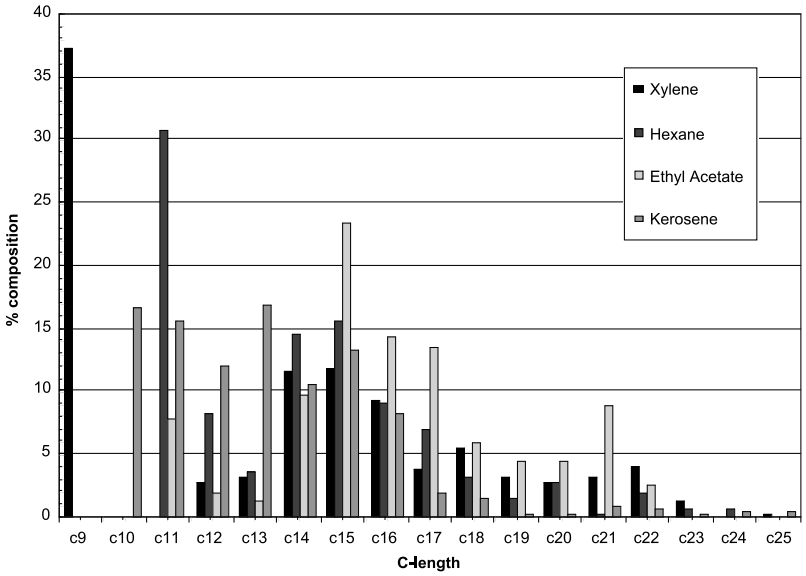


***Figure 3.*** Aliphatic hydrocarbon distribution in extracted oil from the sludge using various solvents.

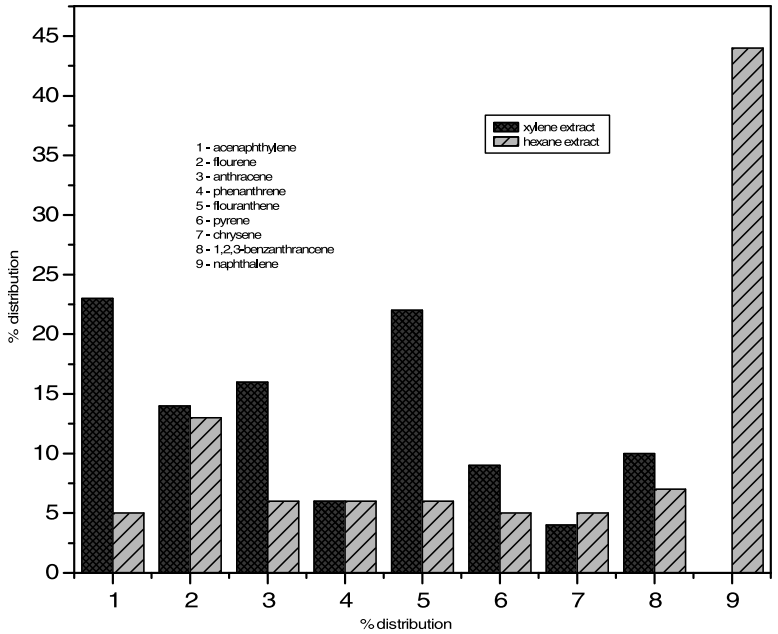


***Figure 4.*** Aromatic hydrocarbon distribution in extracted sludge sample.

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oil, while kerosene (62.55%) showed the least extraction efficiency. The chemical analysis showed the aromatic-aliphatic hydrocarbon ratio in the range of 1.22–6.51 (Table 2). From the results, large quantities of aromatic hydrocarbon were present in the sludge. Since the Escravos oil sludge contains a higher percentage of aromatic hydrocarbons, it is an aromatic sludge. This corroborates the API gravity results.

GC analysis of the extract shows that the oil sludge contains hydrocarbons in the range $C_9$–$C_{28}$. The aliphatic peaks in the extract's chromatograms were readily identified by elution time. The peak number identification included both group number (carbon number) and retention time, and thus defined an exact location on the chromatogram. The aliphatic hydrocarbon content was generally low; the most prominent were $C_{17}$, $C_{18}$, $C_{19}$, and $C_{23}$, while $C_9$, $C_{12}$, $C_{13}$, $C_{14}$, $C_{15}$, $C_{16}$, $C_{20}$, and $C_{21}$ were present in low quantities. $C_{10}$, $C_{11}$, $C_{22}$, $C_{24}$, $C_{25}$, and $C_{26}$ were completely absent (Fig. 2). Hydrocarbon content variation with extracting solvent is reported in Figure 3.

The predominant hydrocarbon type in xylene extract was $C_9$, having about 37.43% occurrences, while $C_{25}$ showed the least occurrence. With hexane extraction, $C_{11}$ was the highest (31% occurrence), while $C_{21}$ was the least. Also, $C_{11}$, $C_{16}$, $C_{20}$, and $C_{24}$ showed two different isomers each, $C_{15}$ and $C_{17}$ occurred in three isomeric forms, and $C_{14}$ showed five isomers. The predominant hydrocarbon type in ethyl acetate extract was $C_{15}$ (23.52%), followed by $C_{16}$, $C_{17}$, $C_{14}$, and $C_{21}$, and the least was $C_{12}$. The quantity of each component extracted varied for different solvents. This shows the affinity of solvents for each of the components.

Aromatic hydrocarbon analysis: Acenaphthene was chosen as an internal standard for the PAH analysis and was eluted immediately after the solvent. The aromatic hydrocarbon content was generally high when compared to the aliphatic content of the extracts. Nineteen major peaks were obtained for the hexane extract from the chromatograms in the temperature range of 98–300°C. These were anthracene, phenanthrene, two isomers each of acenaphthylene, flourene, chrysene, and 1,2,3-benzanthrancene, and three isomers each of naphthalene, fluoranthene and pyrene; thus, a total of nine aromatic hydrocarbons were identified. For the xylene extract, 20 peaks were obtained from the chromatograms, consisting of phenanthrene, two isomers each of anthracene, pyrene, and chrysene, three isomers each of acenaphthylene, fluorine, and fluoranthene, and four isomers of 1,2,3-benzanthrancene, giving a total of eight compounds (Figure 4). Unlike the oxidative thermal treatment of sludge products consisting benzene, toluene, ethylbenzene, and xylene (Shie et al., 2001), the identified aromatic components in the extracts were mainly asphaltenes. Their quantities varied with the solvents. This gave credence to the report of Khan (2001).

The solvent extraction technique has a great tendency to reduce sludge contaminants from 100 to 30% water and solid wastes. This method definitely reduces the pollution effects of oil sludge on the environment with the recovery of recyclable hydrocarbons which can boost the national economy.

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With the optimum conditions carefully selected, solvent extraction approaches can significantly mitigate the non-compliance to standard limit (DPR, 1991) of industrial discharge into the environment and the permissible allowances for petroleum oil sludge.

Reclamation of valuable hydrocarbon oil from sludge accumulation in almost its native form will enhance crude oil volumes. The recovery approach to petroleum oil sludge treatment explored in this study can equally serve as precursor to in-situ treatment/cleaning of oil storage facilities, thereby reducing economic losses and out-of-operation periods (i.e., downtime), since there will be a reduction in time requirements for treatment, which is usually longer with bioremediation (Rahman et al., 2003). Adaptation of these findings to a sludge treatment program is currently being studied by our research team.

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## CONCLUSION

Hydrocarbon recovery from Escravos petroleum oil sludge has been carried out using solvent extraction. The sludge is aromatic and contains a high amount of hydrocarbon. Hexane and xylene were very good solvents for the extraction of useful hydrocarbon from the sludge. This study therefore offers basic data for strategic planning on sludge management in the oil industry.

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